

# Rigorous formulation of two-parameter double-hybrid density-functionals

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A two-parameter extension of the density-scaled double hybrid approach of Sharkas *et al.* [J. Chem. Phys. **134**, 064113 (2011)] is presented. It is based on the explicit treatment of a fraction of multideterminantal exact exchange. The connection with conventional double hybrids is made when neglecting density scaling in the correlation functional as well as second-order corrections to the density. In this context, the fraction  $a_c$  of second-order Møller-Plesset (MP2) correlation energy is not necessarily equal to the square of the fraction  $a_x$  of Hartree-Fock exchange. More specifically, it is shown that  $a_c \leq a_x^2$ , a condition that conventional semi-empirical double hybrids actually fulfill. In addition, a new procedure for calculating the orbitals, which has a better justification than the one routinely used, is proposed. Referred to as  $\lambda_1$  variant, the corresponding double hybrid approximation has been tested on a small set consisting of  $H_2$ ,  $N_2$ ,  $Be_2$ ,  $Mg_2$  and  $Ar_2$ . Three conventional double hybrids (B2-PLYP, B2GP-PLYP and PBE0-DH) have been considered. Potential curves obtained with  $\lambda_1$ - and regular double hybrids can, in some cases, differ significantly. In particular, for the weakly bound dimers, the  $\lambda_1$  variants bind systematically more than the regular ones, which is an improvement in many but not all cases. Including density scaling in the correlation functionals may of course change the results significantly. Moreover, optimized effective potentials (OEPs) based on a partially-interacting system could also be used to generate proper orbitals. Work is currently in progress in those directions.

## I. INTRODUCTION

Sharkas *et al.*<sup>?</sup> recently proposed a rigorous formulation of one-parameter double hybrid density-functionals, which is based on the combination of second-order Møller-Plesset (MP2) perturbation theory with a density-scaled correlation functional. The connection with regular double hybrids<sup>?</sup> could be made when neglecting density scaling. Note that, in their approach, the fraction  $a_c$  of MP2 correlation energy equals the square of the fraction  $a_x$  of Hartree-Fock (HF) exchange. Such a condition is actually not fulfilled by conventional double hybrids. The  $a_c$  parameter is either chosen irrespective of  $a_x$  or expressed in terms of  $a_x$  but *not as*  $a_c = a_x^2$ . In the latter case, one can for example refer to the Perdew-Burke-Ernzerhof-zero double hybrid (PBE0-DH) functional of Brémond and Adamo<sup>?</sup>, which is characterized by  $a_c = a_x^3$ .

This work deals with the rigorous formulation of density-scaled two-parameter double hybrids. It is organized as follows: an *exact* two-parameter energy expression is firstly derived in Sec. II A. Approximate formulations are then investigated for defining single hybrid (Sec. II B) and double hybrid (Sec. II C) energy expressions. In Sec. II D, the connection with conventional double hybrids is made. In addition, a new procedure for computing orbitals is proposed, defining thus what is referred to as  $\lambda_1$  variant of the double hybrids. A summary of the different approximations that have been formulated is then given in Sec. II E. Following the computational details (Sec. III), results obtained with regular

and  $\lambda_1$ -double hybrids on a small test set consisting of  $H_2$ ,  $N_2$ ,  $Be_2$ ,  $Mg_2$  and  $Ar_2$  are presented and discussed in Sec. IV.

## II. THEORY

### A. Multideterminantal exact exchange

The approach recently proposed by Sharkas *et al.*<sup>?</sup> for deriving rigorous one-parameter double-hybrid functionals is based on the separation of the universal Hohenberg-Kohn<sup>?</sup> functional  $F[n] = F^{\lambda_1}[n] + \bar{E}_{\text{Hxc}}^{\lambda_1}[n]$  into a partially-interacting contribution

$$\begin{aligned} F^{\lambda_1}[n] &= \min_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \lambda_1 \hat{W}_{ee} | \Psi \rangle \\ &= \langle \Psi^{\lambda_1}[n] | \hat{T} + \lambda_1 \hat{W}_{ee} | \Psi^{\lambda_1}[n] \rangle, \end{aligned} \quad (1)$$

with  $0 \leq \lambda_1 \leq 1$ , and the *complement*  $\lambda_1$ -dependent Hartree-exchange-correlation (Hxc) density-functional

$$\begin{aligned} \bar{E}_{\text{Hxc}}^{\lambda_1}[n] &= (1 - \lambda_1) E_{\text{Hx}}[n] + \bar{E}_c^{\lambda_1}[n], \\ \bar{E}_c^{\lambda_1}[n] &= E_c[n] - E_c^{\lambda_1}[n], \end{aligned} \quad (2)$$

where  $E_{\text{Hx}}[n] = \langle \Phi^{\text{KS}}[n] | \hat{W}_{ee} | \Phi^{\text{KS}}[n] \rangle$  is the usual exact Hartree-exchange (Hx) term based on the non-interacting Kohn-Sham (KS) determinant<sup>?</sup>. The correlation functionals  $E_c[n]$  and  $E_c^{\lambda_1}[n]$  correspond to fully and partially

$\lambda_1$ -interacting systems, respectively. The exact ground-state energy is then expressed as follows, according to the variational principle<sup>?</sup>,

$$E = \min_n \left\{ \langle \Psi^{\lambda_1}[n] | \hat{T} + \lambda_1 \hat{W}_{ee} + \hat{V}_{ne} | \Psi^{\lambda_1}[n] \rangle + \bar{E}_{\text{Hxc}}^{\lambda_1}[n] \right\}, \quad (3)$$

where  $\hat{V}_{ne} = \int d\mathbf{r} v_{ne}(\mathbf{r}) \hat{n}(\mathbf{r})$  is the nuclear potential operator. Rewritten in terms of a minimization over wave functions, Eq. (3) becomes

$$E = \min_{\Psi} \left\{ \langle \Psi | \hat{T} + \lambda_1 \hat{W}_{ee} + \hat{V}_{ne} | \Psi \rangle + \bar{E}_{\text{Hxc}}^{\lambda_1}[n_{\Psi}] \right\} \quad (4)$$

$$= \langle \Psi^{\lambda_1} | \hat{T} + \lambda_1 \hat{W}_{ee} + \hat{V}_{ne} | \Psi^{\lambda_1} \rangle + \bar{E}_{\text{Hxc}}^{\lambda_1}[n_{\Psi^{\lambda_1}}],$$

where  $\Psi^{\lambda_1}$  fulfills the self-consistent equation

$$\left( \hat{T} + \lambda_1 \hat{W}_{ee} + \hat{V}_{ne} + \hat{V}_{\text{Hxc}}^{\lambda_1}[n_{\Psi^{\lambda_1}}] \right) | \Psi^{\lambda_1} \rangle = \mathcal{E}^{\lambda_1} | \Psi^{\lambda_1} \rangle, \quad (5)$$

$$\hat{V}_{\text{Hxc}}^{\lambda_1}[n] = \int d\mathbf{r} \frac{\delta \bar{E}_{\text{Hxc}}^{\lambda_1}[n]}{\delta n(\mathbf{r})} \hat{n}(\mathbf{r}).$$

In order to introduce a second scaling factor  $\lambda_2$ , and thus derive two-parameter double hybrids, let us consider the following partitioning of the *complement*  $\lambda_1$ -Hxc functional:

$$\bar{E}_{\text{Hxc}}^{\lambda_1}[n] = \bar{E}_{\text{Hx,md}}^{\lambda_1}[n] + \bar{E}_{\text{c,md}}^{\lambda_1}[n], \quad (6)$$

which is based on the multideterminantal definition of the exact exchange (mdEXX), as introduced by Toulouse, Gori-Giorgi and Savin<sup>???</sup> in the context of range-separated density-functional theory (DFT),

$$\bar{E}_{\text{Hx,md}}^{\lambda_1}[n] = (1 - \lambda_1) \langle \Psi^{\lambda_1}[n] | \hat{W}_{ee} | \Psi^{\lambda_1}[n] \rangle. \quad (7)$$

The corresponding *complement* correlation functional differs therefore from the one given in Eq. (2): according to Eqs. (6) and (7) it can be expressed as

$$\bar{E}_{\text{c,md}}^{\lambda_1}[n] = \bar{E}_{\text{c}}^{\lambda_1}[n] - (1 - \lambda_1) \Delta_{\text{c}}^{\lambda_1}[n], \quad (8)$$

$$\Delta_{\text{c}}^{\lambda_1}[n] = \left( \langle \Psi^{\lambda_1}[n] | \hat{W}_{ee} | \Psi^{\lambda_1}[n] \rangle - \langle \Phi^{\text{KS}}[n] | \hat{W}_{ee} | \Phi^{\text{KS}}[n] \rangle \right).$$

Recombined with Eq. (3), Eq. (7) leads to the explicit calculation of 100 % of mdEXX. In the spirit of usual hybrid functionals, we want to keep the flexibility of treating only a fraction  $\lambda_2$  ( $0 \leq \lambda_2 \leq 1$ ) of mdEXX explicitly. For that purpose, we split the *complement* mdHx functional as follows:

$$\bar{E}_{\text{Hx,md}}^{\lambda_1}[n] = (\lambda_2 - \lambda_1) \langle \Psi^{\lambda_1}[n] | \hat{W}_{ee} | \Psi^{\lambda_1}[n] \rangle + (1 - \lambda_2) \langle \Psi^{\lambda_1}[n] | \hat{W}_{ee} | \Psi^{\lambda_1}[n] \rangle, \quad (9)$$

and introduce the *complement*  $\lambda_1$ - and  $\lambda_2$ -dependent Hxc density-functional energy:

$$\begin{aligned} \bar{E}_{\text{Hxc}}^{\lambda_1, \lambda_2}[n] &= (1 - \lambda_2) \langle \Psi^{\lambda_1}[n] | \hat{W}_{ee} | \Psi^{\lambda_1}[n] \rangle + \bar{E}_{\text{c,md}}^{\lambda_1}[n] \\ &= -(\lambda_2 - \lambda_1) \langle \Psi^{\lambda_1}[n] | \hat{W}_{ee} | \Psi^{\lambda_1}[n] \rangle \\ &\quad + \bar{E}_{\text{Hx,md}}^{\lambda_1}[n] + \bar{E}_{\text{c,md}}^{\lambda_1}[n], \end{aligned} \quad (10)$$

which, according to Eqs. (6) and (8), can be rewritten as

$$\begin{aligned} \bar{E}_{\text{Hxc}}^{\lambda_1, \lambda_2}[n] &= -(\lambda_2 - \lambda_1) \langle \Psi^{\lambda_1}[n] | \hat{W}_{ee} | \Psi^{\lambda_1}[n] \rangle + \bar{E}_{\text{Hxc}}^{\lambda_1}[n] \\ &= (1 - \lambda_2) E_{\text{Hx}}[n] + \bar{E}_{\text{c}}^{\lambda_1}[n] \\ &\quad + (\lambda_1 - \lambda_2) \Delta_{\text{c}}^{\lambda_1}[n]. \end{aligned} \quad (11)$$

Using the following expressions based on a uniform coordinate scaling of the density<sup>??</sup>:

$$\begin{aligned} E_{\text{c}}^{\lambda_1}[n] &= \lambda_1^2 E_{\text{c}}[n_{1/\lambda_1}], \\ \Delta_{\text{c}}^{\lambda_1}[n] &= \left. \frac{\partial E_{\text{c}}^{\lambda}[n]}{\partial \lambda} \right|_{\lambda=\lambda_1}, \end{aligned} \quad (12)$$

$$n_{1/\lambda_1}(\mathbf{r}) = (1/\lambda_1)^3 n(\mathbf{r}/\lambda_1),$$

as well as Eq. (2), the more explicit *density-scaled two-parameter* (DS2) form

$$\begin{aligned} \bar{E}_{\text{Hxc}}^{\lambda_1, \lambda_2}[n] &= (1 - \lambda_2) E_{\text{Hx}}[n] + E_{\text{c}}[n] - \lambda_1^2 E_{\text{c}}[n_{1/\lambda_1}] \\ &\quad + 2\lambda_1(\lambda_1 - \lambda_2) E_{\text{c}}[n_{1/\lambda_1}] \\ &\quad + \lambda_1^2(\lambda_1 - \lambda_2) \left. \frac{\partial E_{\text{c}}[n_{1/\lambda}]}{\partial \lambda} \right|_{\lambda=\lambda_1}, \end{aligned} \quad (13)$$

is obtained and the *exact* ground-state energy in Eq. (3) can then be rewritten as follows:

$$E = \min_n \left\{ \langle \Psi^{\lambda_1}[n] | \hat{T} + \lambda_2 \hat{W}_{ee} + \hat{V}_{ne} | \Psi^{\lambda_1}[n] \rangle + \bar{E}_{\text{Hxc}}^{\lambda_1, \lambda_2}[n] \right\}, \quad (14)$$

or, in terms of minimization over local potentials,

$$E = \min_v \left\{ \langle \Psi^{\lambda_1}[v] | \hat{T} + \lambda_2 \hat{W}_{ee} + \hat{V}_{ne} | \Psi^{\lambda_1}[v] \rangle + \bar{E}_{\text{Hxc}}^{\lambda_1, \lambda_2}[n_{\Psi^{\lambda_1}[v]}] \right\}, \quad (15)$$

where  $\Psi^{\lambda_1}[v]$  denotes the ground state of the  $\lambda_1$ -interacting Hamiltonian  $\hat{T} + \lambda_1 \hat{W}_{ee} + \int d\mathbf{r} v(\mathbf{r}) \hat{n}(\mathbf{r})$ . It is important to notice that, for a fixed  $\lambda_1$  value, the *exact* minimizing potential  $v^{\lambda_1}$  is the one which ensures that the density of  $\Psi^{\lambda_1}[v^{\lambda_1}]$  equals the *exact* ground-state density. Therefore, it *does not* depend on  $\lambda_2$ . When choosing  $\lambda_2 = \lambda_1$ , the minimization over potentials in Eq. (15) can be replaced by a minimization over wave functions so that

Eq. (4) is recovered and, according to Eq. (5), the *exact* potential  $v^{\lambda_1}$  can be expressed as

$$v^{\lambda_1}(\mathbf{r}) = v_{\text{ne}}(\mathbf{r}) + \frac{\delta \bar{E}_{\text{Hxc}}^{\lambda_1}}{\delta n(\mathbf{r})} [n_{\Psi^{\lambda_1}}]. \quad (16)$$

As a result, for any  $\lambda_1$  and  $\lambda_2$  values, the *exact* ground-state energy can be written as

$$E = \langle \Psi^{\lambda_1} | \hat{T} + \lambda_2 \hat{W}_{ee} + \hat{V}_{\text{ne}} | \Psi^{\lambda_1} \rangle + \bar{E}_{\text{Hxc}}^{\lambda_1, \lambda_2} [n_{\Psi^{\lambda_1}}]. \quad (17)$$

If  $\lambda_2 \neq \lambda_1$ , the energy cannot be obtained straightforwardly from a minimization over wave functions:

$$E \neq \min_{\Psi} \left\{ \langle \Psi | \hat{T} + \lambda_2 \hat{W}_{ee} + \hat{V}_{\text{ne}} | \Psi \rangle + \bar{E}_{\text{Hxc}}^{\lambda_1, \lambda_2} [n_{\Psi}] \right\}, \quad (18)$$

since the minimizing wave function would be eigenfunction of a  $\lambda_2$ -interacting system and therefore could not be equal to  $\Psi^{\lambda_1}$ , which is eigenfunction of a  $\lambda_1$ -interacting system. As discussed in Sec. II B, it is in principle possible to adapt regular optimized effective potential (OEP) methods to this context in order to implement Eq. (15).

## B. Density-scaled two-parameter single hybrids

This section deals with the formulation of single hybrid functionals based on the energy expression given in Eq. (15). The latter can be considered as a generalization of the standard OEP approach, which is based on a non-interacting KS system, since  $\Psi^{\lambda_1}[v]$  is the ground state of a partially-interacting system. In principle, any wave-function-theory-based model can thus be combined rigorously with OEPs. We consider in this work the optimization of the potential using the HF approximation  $\Phi^{\lambda_1}[v]$  to the exact wave function  $\Psi^{\lambda_1}[v]$ . Following the terminology of Sharkas *et al.*<sup>7</sup>, we refer to this approach as DS2-HF-OEP approximation. In this case, the energy becomes

$$E_{\text{HF-OEP}}^{\text{DS2}, \lambda_1, \lambda_2} = \min_v E_{\text{HF-OEP}}^{\text{DS2}, \lambda_1, \lambda_2} [v],$$

$$E_{\text{HF-OEP}}^{\text{DS2}, \lambda_1, \lambda_2} [v] = \left\{ \langle \Phi^{\lambda_1}[v] | \hat{T} + \lambda_2 \hat{W}_{ee} + \hat{V}_{\text{ne}} | \Phi^{\lambda_1}[v] \rangle + \bar{E}_{\text{Hxc}}^{\lambda_1, \lambda_2} [n_{\Phi^{\lambda_1}[v]}] \right\}. \quad (19)$$

Such an approach can be interpreted as an exchange-only-type OEP calculation based on a  $\lambda_1$ -interacting system. As a result, the DS2-HF-OEP energy gradient has no simple analytical expression, like in the KS-OEP scheme<sup>7</sup>. However, it can be efficiently computed from a HF-type linear response vector, using a decomposition of the potential in an auxiliary basis of gaussian functions.

Work is currently in progress in this direction. If we simply denote  $\Phi$  and  $n$  the converged DS2-HF-OEP determinant and its density, the energy can be reexpressed, according to Eq. (13), as

$$E_{\text{HF-OEP}}^{\text{DS2}, \lambda_1, \lambda_2} = \langle \Phi | \hat{T} + \hat{V}_{\text{ne}} | \Phi \rangle + E_{\text{H}}[n] + \lambda_2 E_{\text{x}}^{\text{HF}}[\Phi] + (1 - \lambda_2) E_{\text{x}}[n] + E_{\text{c}}[n] - \lambda_1 (2\lambda_2 - \lambda_1) E_{\text{c}}[n_{1/\lambda_1}] + \lambda_1^2 (\lambda_1 - \lambda_2) \left. \frac{\partial E_{\text{c}}[n_{1/\lambda}]}{\partial \lambda} \right|_{\lambda=\lambda_1}, \quad (20)$$

where  $E_{\text{x}}^{\text{HF}}[\Phi]$  is the HF exchange energy. We thus obtain a *density-scaled two-parameter hybrid* (DS2H) exchange-correlation energy:

$$E_{\text{xc}, \text{DS2H}}^{\lambda_1, \lambda_2} = \lambda_2 E_{\text{x}}^{\text{HF}}[\Phi] + (1 - \lambda_2) E_{\text{x}}[n] + E_{\text{c}}[n] - \lambda_1 (2\lambda_2 - \lambda_1) E_{\text{c}}[n_{1/\lambda_1}] + \lambda_1^2 (\lambda_1 - \lambda_2) \left. \frac{\partial E_{\text{c}}[n_{1/\lambda}]}{\partial \lambda} \right|_{\lambda=\lambda_1}. \quad (21)$$

Note that, in the particular case  $\lambda_1 = \lambda_2$ , the *exact* DS2-HF-OEP potential can be expressed in terms of a functional derivative like in the exact theory (see Sec. II A). Indeed, the DS2-Hxc functional in Eq. (13) reduces then to a DS1-Hxc functional which corresponds to the *complement*  $\lambda_1$ -Hxc functional:

$$\bar{E}_{\text{Hxc}}^{\lambda_1, \lambda_1} [n] = (1 - \lambda_1) E_{\text{Hxc}}[n] + E_{\text{c}}[n] - \lambda_1^2 E_{\text{c}}[n_{1/\lambda_1}] = \bar{E}_{\text{Hxc}}^{\lambda_1} [n]. \quad (22)$$

Moreover, using the *one-to-one* correspondance between the density  $n_{\Phi}$  of any single determinant  $\Phi$  and the local potential  $v^{\lambda_1}[n_{\Phi}]$  such that the density of the HF determinant  $\Phi^{\lambda_1}[v^{\lambda_1}[n_{\Phi}]]$  equals  $n_{\Phi}$ , the energy in Eq. (19) can be simply obtained by minimization over single determinants, that is without using OEPs. It then corresponds to the DS1H energy of Sharkas *et al.*<sup>7</sup> which equals

$$E_{\text{DS1H}}^{\lambda_1} = \min_{\Phi} \left\{ \langle \Phi | \hat{T} + \lambda_1 \hat{W}_{ee} + \hat{V}_{\text{ne}} | \Phi \rangle + \bar{E}_{\text{Hxc}}^{\lambda_1} [n_{\Phi}] \right\} \quad (23)$$

The minimizing determinant  $\Phi^{\lambda_1}$  fulfills the self-consistent equation

$$\left( \hat{T} + \lambda_1 \hat{U}_{\text{HF}}[\Phi^{\lambda_1}] + \hat{V}_{\text{ne}} + \hat{V}_{\text{Hxc}}^{\lambda_1} [n_{\Phi^{\lambda_1}}] \right) | \Phi^{\lambda_1} \rangle = \mathcal{E}_{\text{DS1H}}^{\lambda_1} | \Phi^{\lambda_1} \rangle, \quad (24)$$

where  $\hat{U}_{\text{HF}}[\Phi^{\lambda_1}]$  is the nonlocal HF potential, so that, in this particular case, the minimizing potential in Eq. (19) can be expressed as

$$v_{\text{DS1H}}^{\lambda_1}(\mathbf{r}) = v_{\text{ne}}(\mathbf{r}) + \frac{\delta \bar{E}_{\text{Hxc}}^{\lambda_1}}{\delta n(\mathbf{r})} [n_{\Phi^{\lambda_1}}], \quad (25)$$

and the exchange-correlation in Eq. (21) reduces to

$$E_{\text{xc,DS1H}}^{\lambda_1} = \lambda_1 E_{\text{x}}^{\text{HF}}[\Phi] + (1 - \lambda_1) E_{\text{x}}[n] + E_{\text{c}}[n] - \lambda_1^2 E_{\text{c}}[n_{1/\lambda_1}]. \quad (26)$$

### C. Density-scaled two-parameter double hybrids

This section deals with the formulation of double hybrid functionals based on the energy expression given in Eq. (15). In the following, we denote  $v_0^{\lambda_1}$  any approximation to the exact minimizing potential  $v^{\lambda_1}$ . An approximate expression for the energy is thus obtained:

$$E_0^{\lambda_1, \lambda_2} = \langle \Psi_0^{\lambda_1} | \hat{T} + \lambda_2 \hat{W}_{ee} + \hat{V}_{ne} | \Psi_0^{\lambda_1} \rangle + \bar{E}_{\text{Hxc}}^{\lambda_1, \lambda_2} [n_{\Psi_0^{\lambda_1}}] \quad (27)$$

where  $\Psi_0^{\lambda_1}$  is the ground state of the  $\lambda_1$ -interacting system defined by  $v_0^{\lambda_1}$ :

$$(\hat{T} + \lambda_1 \hat{W}_{ee} + \hat{V}_0^{\lambda_1}) | \Psi_0^{\lambda_1} \rangle = \mathcal{E}_0^{\lambda_1} | \Psi_0^{\lambda_1} \rangle, \quad (28)$$

with  $\hat{V}_0^{\lambda_1} = \int d\mathbf{r} v_0^{\lambda_1}(\mathbf{r}) \hat{n}(\mathbf{r})$ . The energy in Eq. (27) can be rewritten as

$$\begin{aligned} E_0^{\lambda_1, \lambda_2} &= \mathcal{E}_0^{\lambda_1} + (\lambda_2 - \lambda_1) \langle \Psi_0^{\lambda_1} | \hat{W}_{ee} | \Psi_0^{\lambda_1} \rangle \\ &\quad + \langle \Psi_0^{\lambda_1} | \hat{V}_{ne} - \hat{V}_0^{\lambda_1} | \Psi_0^{\lambda_1} \rangle \\ &\quad + \bar{E}_{\text{Hxc}}^{\lambda_1, \lambda_2} [n_{\Psi_0^{\lambda_1}}], \end{aligned} \quad (29)$$

which is convenient when applying, as we propose in the following, MP perturbation theory to the  $\lambda_1$ -interacting system described by Eq. (28). The zeroth-order wave function is chosen to be the determinant  $\Phi_0^{\lambda_1}$  which fulfills the HF-type equation

$$(\hat{T} + \lambda_1 \hat{U}_{\text{HF}}[\Phi_0^{\lambda_1}] + \hat{V}_0^{\lambda_1}) | \Phi_0^{\lambda_1} \rangle = \mathcal{E}_{\text{HF}}^{\lambda_1} | \Phi_0^{\lambda_1} \rangle. \quad (30)$$

Note that the Brillouin theorem is fulfilled in this context, which means that the wave function contains only double excitations through first order and, as a result, the density remains unchanged through first order<sup>?</sup>. The perturbation expansion of the fictitious  $\lambda_1$ -interacting energy through second order equals:

$$\mathcal{E}_0^{\lambda_1} = \langle \Phi_0^{\lambda_1} | \hat{T} + \lambda_1 \hat{W}_{ee} + \hat{V}_0^{\lambda_1} | \Phi_0^{\lambda_1} \rangle + \lambda_1^2 E_{\text{MP}}^{(2)} + \dots, \quad (31)$$

where  $E_{\text{MP}}^{(2)}$  is the conventional MP2 energy correction calculated with the  $\lambda_1$ -interacting orbitals and orbital energies obtained from Eq. (30). Using the simplified perturbation expansion for the second term in the right-hand side of Eq. (29):

$$\langle \Psi_0^{\lambda_1} | \hat{W}_{ee} | \Psi_0^{\lambda_1} \rangle = \langle \Phi_0^{\lambda_1} | \hat{W}_{ee} | \Phi_0^{\lambda_1} \rangle + 2\lambda_1 E_{\text{MP}}^{(2)} + \dots, \quad (32)$$

we obtain the final energy expression through second order:

$$\begin{aligned} E_0^{\lambda_1, \lambda_2} &= \langle \Phi_0^{\lambda_1} | \hat{T} + \lambda_2 \hat{W}_{ee} + \hat{V}_{ne} | \Phi_0^{\lambda_1} \rangle \\ &\quad + \bar{E}_{\text{Hxc}}^{\lambda_1, \lambda_2} [n_{\Phi_0^{\lambda_1}}] + \lambda_1 (2\lambda_2 - \lambda_1) E_{\text{MP}}^{(2)} \\ &\quad + \int d\mathbf{r} \left( v_{\text{ne}}(\mathbf{r}) - v_0^{\lambda_1}(\mathbf{r}) + \frac{\delta \bar{E}_{\text{Hxc}}^{\lambda_1, \lambda_2}}{\delta n(\mathbf{r})} [n_{\Phi_0^{\lambda_1}}] \right) \delta n^{(2)}(\mathbf{r}) \\ &\quad + \dots, \end{aligned} \quad (33)$$

where  $\delta n^{(2)}(\mathbf{r})$  denotes the second-order correction to the density associated to  $\Psi_0^{\lambda_1}$ . If we simply denote  $\Phi$  and  $n$  the zeroth-order determinant  $\Phi_0^{\lambda_1}$  and its density, respectively, the exchange-correlation energy has, according to Eq. (13), the form of a *density scaled two-parameter double hybrid* (DS2DH) functional:

$$\begin{aligned} E_{\text{xc,DS2DH}}^{\lambda_1, \lambda_2} &= \lambda_2 E_{\text{x}}^{\text{HF}}[\Phi] + (1 - \lambda_2) E_{\text{x}}[n] + E_{\text{c}}[n] \\ &\quad - \lambda_1 (2\lambda_2 - \lambda_1) E_{\text{c}}[n_{1/\lambda_1}] \\ &\quad + \lambda_1^2 (\lambda_1 - \lambda_2) \left. \frac{\partial E_{\text{c}}[n_{1/\lambda}]}{\partial \lambda} \right|_{\lambda=\lambda_1} \\ &\quad + \lambda_1 (2\lambda_2 - \lambda_1) E_{\text{MP}}^{(2)} \\ &\quad + \int d\mathbf{r} \left( v_{\text{ne}}(\mathbf{r}) - v_0^{\lambda_1}(\mathbf{r}) + \frac{\delta \bar{E}_{\text{Hxc}}^{\lambda_1, \lambda_2}}{\delta n(\mathbf{r})} [n] \right) \delta n^{(2)}(\mathbf{r}). \end{aligned} \quad (34)$$

Let us consider the particular case  $\lambda_1 = \lambda_2$ . According to Eqs. (22) and (25), when choosing the DS1H determinant  $\Phi^{\lambda_1}$  and potential  $v_{\text{DS1H}}^{\lambda_1}$  as  $\Phi$  and  $v_0^{\lambda_1}$ , the second-order-density-correction term in the right-hand side of Eq. (34) cancels out and the DS1DH exchange-correlation energy of Sharkas *et al.*<sup>?</sup> is recovered:

$$\begin{aligned} E_{\text{xc,DS1DH}}^{\lambda_1} &= \lambda_1 E_{\text{x}}^{\text{HF}}[\Phi] + (1 - \lambda_1) E_{\text{x}}[n] + E_{\text{c}}[n] \\ &\quad - \lambda_1^2 E_{\text{c}}[n_{1/\lambda_1}] + \lambda_1^2 E_{\text{MP}}^{(2)}. \end{aligned} \quad (35)$$

As shown in Sec. IID, the DS2DH functional defined in Eq. (34) can be connected with conventional double hybrids when neglecting both second-order corrections to the density as well as the density scaling in the correlation functional.

### D. Connection with conventional double hybrids

In order to connect regular double hybrids with the one derived in Sec. IIC, we neglect both second-order corrections to the density as well as the density scaling

in the correlation functional:

$$\delta n^{(2)}(\mathbf{r}) \approx 0, \quad E_c[n_{1/\lambda}] \approx E_c[n]. \quad (36)$$

The DS2H and DS2DH exchange-correlation energies in Eqs. (21) and (34) reduce then to *two-parameter hybrid* (2H) and *two-parameter double hybrid* (2DH) exchange-correlation energies, respectively:

$$E_{\text{xc},2\text{H}}^{a_x,a_c} = a_x E_{\text{x}}^{\text{HF}}[\Phi] + (1 - a_x) E_{\text{x}}[n] + (1 - a_c) E_c[n], \quad (37)$$

and

$$E_{\text{xc},2\text{DH}}^{a_x,a_c} = a_x E_{\text{x}}^{\text{HF}}[\Phi] + (1 - a_x) E_{\text{x}}[n] + (1 - a_c) E_c[n] + a_c E_{\text{MP}}^{(2)}, \quad (38)$$

where we have introduced the two parameters  $a_x$  and  $a_c$  defined as follows:

$$\begin{aligned} a_x &= \lambda_2, \\ a_c &= \lambda_1(2\lambda_2 - \lambda_1) \\ &= a_x^2 - (a_x - \lambda_1)^2. \end{aligned} \quad (39)$$

Let us first notice that, by contrast to KS second-order perturbation theory<sup>7</sup> (KS-PT2), single excitations do not appear in the 2DH energy expression. Indeed, the latter originates from a MP-type calculation, where the Brillouin theorem therefore applies, and which is based on a partially  $\lambda_1$ -interacting system. In addition, it is readily seen from Eq. (39) that, in this context,  $a_c \leq a_x^2$ . Interestingly, the various conventional double hybrids considered in Table I fulfill this condition. Note that the *one-parameter double hybrid* (1DH) approximation<sup>7</sup> is recovered when  $\lambda_1 = \lambda_2$ , or, in terms of  $a_x$  and  $a_c$ ,  $a_c = a_x^2$ . For given values of  $\lambda_1$  and  $\lambda_2$ , a unique set of  $a_x$  and  $a_c$  parameters can be defined according to Eq. (39). Reciprocally, for given  $a_x$  and  $a_c$  values, we can define the two scaling factors  $\lambda_1$  and  $\lambda_2$  as follows:

$$\begin{aligned} \lambda_2 &= a_x, \\ \lambda_1 &= a_x \pm \sqrt{a_x^2 - a_c}. \end{aligned} \quad (40)$$

When  $a_c = 0$ , the correlation energy is fully described by the correlation functional which means that the fictitious  $\lambda_1$ -interacting system should be the non-interacting (KS) one, that is  $\lambda_1 = 0$ . The standard exchange-only-type KS-OEP scheme with  $a_x$  as fraction of exact exchange is thus recovered. We therefore conclude

$$\lambda_1 = a_x - \sqrt{a_x^2 - a_c}. \quad (41)$$

Interestingly, the *linearly scaled one-parameter double hybrid* functional (LS1DH) derived recently by Toulouse *et al.*<sup>7</sup>, which is characterized by  $a_c = a_x^3$ , is recovered here, though density scaling is neglected, when  $\lambda_1$  equals

$$\lambda_1^{\text{LS1DH}} = a_x(1 - \sqrt{1 - a_x}). \quad (42)$$

Let us now focus on the calculation of the orbitals. As pointed out in Sec. II C, the DS2DH and thus the 2DH exchange-correlation energies are based on HF-type orbitals calculated for a  $\lambda_1$ -interacting system. A natural choice of orbitals would therefore be the DS2-HF-OEP ones. Since density scaling is neglected, we will refer to them as  $\lambda_1$ -OEP-2H orbitals and the corresponding 2DH energy will be referred to as  $\lambda_1$ -OEP-2DH. The  $\lambda_1$ -OEP-2H scheme, which is an OEP-type calculation, can be formulated as follows, according to Eqs. (13), (19) and (36) and (39):

$$\begin{aligned} E_{\lambda_1\text{-OEP-2H}}^{a_x,a_c} &= \min_v E_{\lambda_1\text{-OEP-2H}}^{a_x,a_c}[v], \\ E_{\lambda_1\text{-OEP-2H}}^{a_x,a_c}[v] &= \left\{ \langle \Phi^{\lambda_1}[v] | \hat{T} + \hat{V}_{\text{ne}} | \Phi^{\lambda_1}[v] \rangle \right. \\ &\quad \left. + E_{\text{H}}[n_{\Phi^{\lambda_1}}[v]] + a_x E_{\text{x}}^{\text{HF}}[\Phi^{\lambda_1}[v]] \right. \\ &\quad \left. + (1 - a_x) E_{\text{x}}[n_{\Phi^{\lambda_1}}[v]] + (1 - a_c) E_c[n_{\Phi^{\lambda_1}}[v]] \right\}, \end{aligned} \quad (43)$$

where  $\Phi^{\lambda_1}[v]$  fulfills the  $\lambda_1$ -interacting HF equation

$$\left( \hat{T} + \lambda_1 \hat{U}_{\text{HF}}[\Phi^{\lambda_1}[v]] + \hat{V} \right) |\Phi^{\lambda_1}[v]\rangle = \mathcal{E}_{\text{HF}}^{\lambda_1}[v] |\Phi^{\lambda_1}[v]\rangle, \quad (44)$$

with  $\hat{V} = \int d\mathbf{r} v(\mathbf{r}) \hat{n}(\mathbf{r})$  and  $\lambda_1$  defined in Eq. (41). On the hand, for conventional double hybrids, the orbitals are obtained from a 2H calculation which can be formulated as?

$$\begin{aligned} E_{2\text{H}}^{a_x,a_c} &= \min_{\Phi} \left\{ \langle \Phi | \hat{T} + \hat{V}_{\text{ne}} | \Phi \rangle + E_{\text{H}}[n_{\Phi}] + a_x E_{\text{x}}^{\text{HF}}[\Phi] \right. \\ &\quad \left. + (1 - a_x) E_{\text{x}}[n_{\Phi}] + (1 - a_c) E_c[n_{\Phi}] \right\}. \end{aligned} \quad (45)$$

The minimizing determinant  $\tilde{\Phi}$  in Eq. (45) fulfills the 2H equation

$$\begin{aligned} \left( \hat{T} + \hat{V}_{\text{ne}} + a_x \hat{U}_{\text{HF}}[\tilde{\Phi}] + (1 - a_x) \hat{V}_{\text{Hx}}[n_{\tilde{\Phi}}] \right. \\ \left. + (1 - a_c) \hat{V}_{\text{c}}[n_{\tilde{\Phi}}] \right) |\tilde{\Phi}\rangle = \mathcal{E}_{2\text{H}} |\tilde{\Phi}\rangle, \end{aligned} \quad (46)$$

and, therefore, can be interpreted as the HF determinant associated to a  $\lambda_2$ -interacting system since, according to Eq. (40),  $\lambda_2 = a_x$ . However, as shown in Sec. II C, the 2DH exchange-correlation functional in Eq. (38) can be justified when it is based on HF-type orbitals associated to a  $\lambda_1$ -interacting Hamiltonian. This condition ensures that single excitations do not contribute to the exchange-correlation energy. In fact, the conventional calculation of the orbitals is simply deduced from Eq. (43) when replacing the minimization over local potentials by a minimization over single determinants, which is justified only when  $\lambda_2 = \lambda_1$  that is equivalent to  $a_c = a_x^2$  (see Sec. II B). As shown in Table I, conventional double hybrids do not fulfill the latter condition. In this respect, double hybrids

based on the  $\lambda_1$ -OEP-2H approximation have a better justification than the regular ones. Let us finally consider a possible alternative to the  $\lambda_1$ -OEP-2H scheme, which would not require the calculation of an OEP and would have a computational cost similar to conventional 2H calculations. As shown in Sec. II A, in the *exact* theory and for a fixed  $\lambda_1$  value, the OEP should not depend on  $\lambda_2$ . As an approximation, referred to as  $\lambda_1$ -2H in the following, we assume that this statement still holds within the *approximate*  $\lambda_1$ -OEP-2H scheme. As a result, an approximate potential can be obtained when choosing, in Eq. (19),  $\lambda_2 = \lambda_1$  instead of  $\lambda_2 = a_x$ . In this particular case, according to Eqs. (22), (24), and (36), the  $\lambda_1$ -2H determinant  $\tilde{\Phi}'$  fulfills the modified 2H equation

$$\begin{aligned} & \left( \hat{T} + \hat{V}_{\text{ne}} + a'_x \hat{U}_{\text{HF}}[\tilde{\Phi}'] + (1 - a'_x) \hat{V}_{\text{Hx}}[n_{\tilde{\Phi}'}] \right. \\ & \left. + (1 - a'_c) \hat{V}_c[n_{\tilde{\Phi}'}] \right) |\tilde{\Phi}'\rangle = \mathcal{E}'_{2\text{H}} |\tilde{\Phi}'\rangle, \end{aligned} \quad (47)$$

where the regular  $a_x$  and  $a_c$  parameters have been replaced by  $\lambda_1$  and  $\lambda_1^2$ , respectively:

$$\begin{aligned} a_x & \rightarrow a'_x = \lambda_1 = a_x - \sqrt{a_x^2 - a_c} \\ a_c & \rightarrow a'_c = \lambda_1^2 = 2a_x \left( a_x - \sqrt{a_x^2 - a_c} \right) - a_c. \end{aligned} \quad (48)$$

We thus ensure that the orbitals are computed from a  $\lambda_1$ -interacting system. This procedure basically consists in approximating the *exact* potential  $v^{\lambda_1}$  by

$$\begin{aligned} v_{\lambda_1-2\text{H}}(\mathbf{r}) &= v_{\text{ne}}(\mathbf{r}) + (1 - a'_x) \frac{\delta E_{\text{Hx}}}{\delta n(\mathbf{r})}[n_{\tilde{\Phi}'}] \\ &+ (1 - a'_c) \frac{\delta E_c}{\delta n(\mathbf{r})}[n_{\tilde{\Phi}'}]. \end{aligned} \quad (49)$$

Using this potential and  $\tilde{\Phi}'$  as  $v_0^{\lambda_1}$  and  $\Phi_0^{\lambda_1}$  in Eq. (33), we obtain from Eqs. (36) and (39) the following expressions for the  $\lambda_1$ -2DH energy:

$$\begin{aligned} E_{\lambda_1-2\text{DH}}^{a_x, a_c} &= \langle \tilde{\Phi}' | \hat{T} + \hat{V}_{\text{ne}} | \tilde{\Phi}' \rangle + E_{\text{H}}[\tilde{n}'] + a_x E_{\text{x}}^{\text{HF}}[\tilde{\Phi}'] \\ &+ (1 - a_x) E_{\text{x}}[\tilde{n}'] \\ &+ (1 - a_c) E_{\text{c}}[\tilde{n}'] + a_c E_{\text{MP}}^{(2)'} \\ &= E_{\lambda_1-2\text{H}}^{a_x, a_c} + a_c E_{\text{MP}}^{(2)'}, \end{aligned} \quad (50)$$

where  $\tilde{n}'$  denotes the density of  $\tilde{\Phi}'$  and  $E_{\text{MP}}^{(2)'}$  is the regular MP2 energy correction calculated with  $\lambda_1$ -2H orbitals and orbital energies. The  $\lambda_1$ -2H and  $\lambda_1$ -2DH exchange-correlation energies are therefore expressed respectively as

$$\begin{aligned} E_{\text{xc}, \lambda_1-2\text{H}}^{a_x, a_c} &= a_x E_{\text{x}}^{\text{HF}}[\tilde{\Phi}'] + (1 - a_x) E_{\text{x}}[\tilde{n}'] \\ &+ (1 - a_c) E_{\text{c}}[\tilde{n}'], \end{aligned} \quad (51)$$

and

$$\begin{aligned} E_{\text{xc}, \lambda_1-2\text{DH}}^{a_x, a_c} &= a_x E_{\text{x}}^{\text{HF}}[\tilde{\Phi}'] + (1 - a_x) E_{\text{x}}[\tilde{n}'] \\ &+ (1 - a_c) E_{\text{c}}[\tilde{n}'] + a_c E_{\text{MP}}^{(2)'}. \end{aligned} \quad (52)$$

Let us stress that the  $\lambda_1$ -2H and  $\lambda_1$ -2DH energies as defined in Eq. (50), and thus the corresponding exchange-correlation energies in Eqs. (51) and (52), are obtained from the same energy expressions as in the regular 2H and 2DH schemes, using standard  $a_x$  and  $a_c$  values. The difference comes from the orbitals which are calculated with the modified  $a'_x$  and  $a'_c$  coefficients.

## E. Summary

A two-parameter extension of the DS1DH scheme proposed recently by Sharkas *et al.*<sup>7</sup> has been derived. It is based on the explicit treatment of a fraction of mdEXX which requires, in the general case, the calculation of an OEP for a partially-interacting system. Computing this OEP at the HF level of approximation leads to the DS2-HF-OEP scheme where the energy has a DS2H form. In addition, it was shown that, using any approximate potential, DS2DHs can be defined. The connection between the latter and regular double hybrids is made when neglecting both second-order corrections to the density and density scaling. In this case, the DS2-HF-OEP approximation reduces to the  $\lambda_1$ -OEP-2H one and the corresponding DS2DH scheme (which is based on the  $\lambda_1$ -OEP-2H potential) is then referred to as  $\lambda_1$ -OEP-2DH. As an alternative to the  $\lambda_1$ -OEP-2H calculation, the  $\lambda_1$ -2H scheme, where the OEP calculation is replaced by a 2H one with modified exchange and correlation coefficients, has been proposed. A  $\lambda_1$ -2DH approximation could thus be defined from the  $\lambda_1$ -OEP-2DH energy expression using  $\lambda_1$ -2H orbitals instead of the  $\lambda_1$ -OEP-2H ones. In this work, only  $\lambda_1$ -2H and  $\lambda_1$ -2DH results will be shown. The OEP-based schemes, which are currently under implementation, will be presented in a separate paper.

## III. COMPUTATIONAL DETAILS

Both  $\lambda_1$ -2H and  $\lambda_1$ -2DH energy expressions in Eq. (50) can be simply implemented using a regular DFT code that can perform double hybrid calculations. A development version<sup>7</sup> of the DALTON program package<sup>7</sup> has been used in this work. In a first step, a  $\lambda_1$ -2H calculation is done. It consists in performing a 2H calculation with the modified exchange and correlation coefficients defined in Eq. (48). The corresponding orbitals and orbital energies are then used, in a second step, to compute the scaled MP2 term. In a third step, the  $\lambda_1$ -2H energy is obtained from a regular one-iteration 2H calculation, using the  $\lambda_1$ -2H orbitals as starting orbitals. Three conventional

double hybrids have been considered: the B2-PLYP<sup>?</sup> and B2GP-PLYP<sup>?</sup> functionals based on the Becke 88 (B) exchange functional and the Lee-Yang-Parr (LYP) correlation functional, and the PBE0-DH<sup>?</sup> functional which is based on the Perdew-Burke-Ernzerhof (PBE) exchange functional<sup>?</sup> and the Perdew-Wang (PW) correlation functional<sup>?</sup>. The corresponding exchange and correlation coefficients are given in Table I. Calculations have been performed on a test set consisting of H<sub>2</sub>, N<sub>2</sub>, Be<sub>2</sub>, Mg<sub>2</sub> and Ar<sub>2</sub>. The following basis sets were used: cc-pVQZ<sup>?</sup> for H<sub>2</sub> and N<sub>2</sub>, aug-cc-pVQZ<sup>?</sup> for Be<sub>2</sub> and Mg<sub>2</sub>, and aug-cc-pVTZ<sup>?</sup> for Ar<sub>2</sub>.

#### IV. RESULTS AND DISCUSSION

In this section we compare, in terms of accuracy, the regular B2-PLYP, B2GP-PLYP and PBE0-DH double hybrids with their  $\lambda_1$  variants, as defined in Sec. IID. The potential curves computed for H<sub>2</sub> and N<sub>2</sub> (see Fig. 1) show a systematic lowering of the total energy when using  $\lambda_1$ -double hybrids instead of the regular ones. This can be analyzed when decomposing the difference between the  $\lambda_1$ -2DH and regular double hybrid energies into a single hybrid term  $\Delta E_{\text{SH}} = E_{\lambda_1\text{-2H}}^{a_x, a_c} - E_{\text{2H}}^{a_x, a_c}$  (see Eqs. (45) and (50)) and a scaled MP2 term  $a_c \Delta E_{\text{MP2}} = a_c (E_{\text{MP}}^{(2)'} - E_{\text{MP}}^{(2)})$  (see Eq. (50)). As illustrated in Fig. 2 (a), for H<sub>2</sub>, the  $\lambda_1$ -2H energy is always greater than the regular 2H one ( $\Delta E_{\text{SH}} \geq 0$ ) which is due to the fact that the  $\lambda_1$ -2H orbitals are not optimized for the regular 2H energy expression (based on  $a_x$  and  $a_c$ ) but for a modified one (based on  $a'_x$  and  $a'_c$ ). This positive difference is then compensated when adding the scaled MP2 contribution. According to Eq. (48), the fraction  $a'_x$  of HF exchange used to compute the  $\lambda_1$ -2H orbitals is lower than the regular fraction  $a_x$ . This leads to a smaller HOMO-LUMO gap (see Fig. 2 (b)) and thus to a larger scaled MP2 correction. Note, however, that B2GP-PLYP gives the largest  $a_c \Delta E_{\text{MP2}}$  term in absolute value while PBE0-DH, for which  $a'_x$  differs the most from  $a_x$ , has the largest reduction (in absolute value) of HOMO-LUMO gap. It could be explained by the fact that the scaled MP2 correction is sensitive not only to the orbital energies but also to the orbitals. Results obtained for N<sub>2</sub> (not shown) lead to the same conclusion. Returning to the potential curves in Fig. 1, we finally note that the  $\lambda_1$  variant slightly improves the accuracy of the double hybrids in the vicinity of the equilibrium distance.

Concerning the weakly-bound systems Be<sub>2</sub>, Mg<sub>2</sub> and Ar<sub>2</sub>, the interaction energy curves in Fig. 3 show that regular double hybrids and their  $\lambda_1$  variants behave similarly at large distances but the latter bind more than the former. This often leads to slightly more accurate results unless the regular double hybrid, like PBE0-DH for Be<sub>2</sub> and Mg<sub>2</sub>, already overbinds. It would of course be interesting to evaluate the effects of density scaling in the correlation functional. Indeed, in the light of Sharkas

*et al.*<sup>?</sup> study, results are expected to change significantly.

#### V. CONCLUSIONS

A rigorous derivation of two-parameter double hybrids (2DHs) has been presented. It is based on the combination of the DS1DH scheme of Sharkas *et al.*<sup>?</sup> with the explicit treatment of a fraction of multideterminantal exact exchange. The connection with regular double hybrids is made when neglecting both density scaling and second-order corrections to the density. It then appears, in this context, that the fraction of second-order Møller-Plesset (MP2) energy correlation is smaller or equal to the square of the fraction of Hartree Fock (HF) exchange. Interestingly, various conventional semi-empirical double hybrids fulfill this condition. In the light of those derivations, a new procedure for calculating the orbitals, which is more justified than the one used routinely, has been proposed. It still consists in performing a two-parameter hybrid calculation, but with modified exchange and correlation coefficients. Preliminary results presented in this work show that, in such a scheme which is referred to as  $\lambda_1$ -2DH, the MP2 energy contribution is, in absolute value, larger than the regular one. As a result,  $\lambda_1$ -2DH and regular double hybrid potential curves can, in some cases, differ significantly. In particular, for the tested weakly bound dimers, the  $\lambda_1$  variants bind systematically more than the regular ones, which is often but not always an improvement. Including density scaling in the correlation functionals may of course change the results significantly. This still needs to be investigated. Moreover, optimized effective potentials (OEPs) based on a partially-interacting system could also be used to generate proper orbitals. Work is currently in progress in those directions.

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## FIGURE CAPTIONS

**Figure 1:** Potential curves for  $\text{H}_2$  (top) and  $\text{N}_2$  (bottom). The "exact" curves are taken from Ref.<sup>?</sup>

**Figure 2:** Single hybrid ( $\Delta E_{\text{SH}}$ ) and scaled MP2 ( $a_c \Delta E_{\text{MP2}}$ ) energy differences between  $\lambda_1$ - and conventional B2-PLYP, B2GP-PLYP and PBE0-DH double hybrids calculated for  $\text{H}_2$  with respect to the bond distance (left); HOMO-LUMO gap for both  $\lambda_1$ - and conventional B2-PLYP, B2GP-PLYP and PBE0-DH double hybrids calculated for  $\text{H}_2$  with respect to the bond distance (right).

**Figure 3:** Interaction energy curves for  $\text{Be}_2$ ,  $\text{Mg}_2$  and  $\text{Ar}_2$ . The accurate<sup>?</sup>, experimental<sup>?</sup> and CCSD(T) curves are taken as reference.



FIG. 1: Fromager, Journal of Chemical Physics

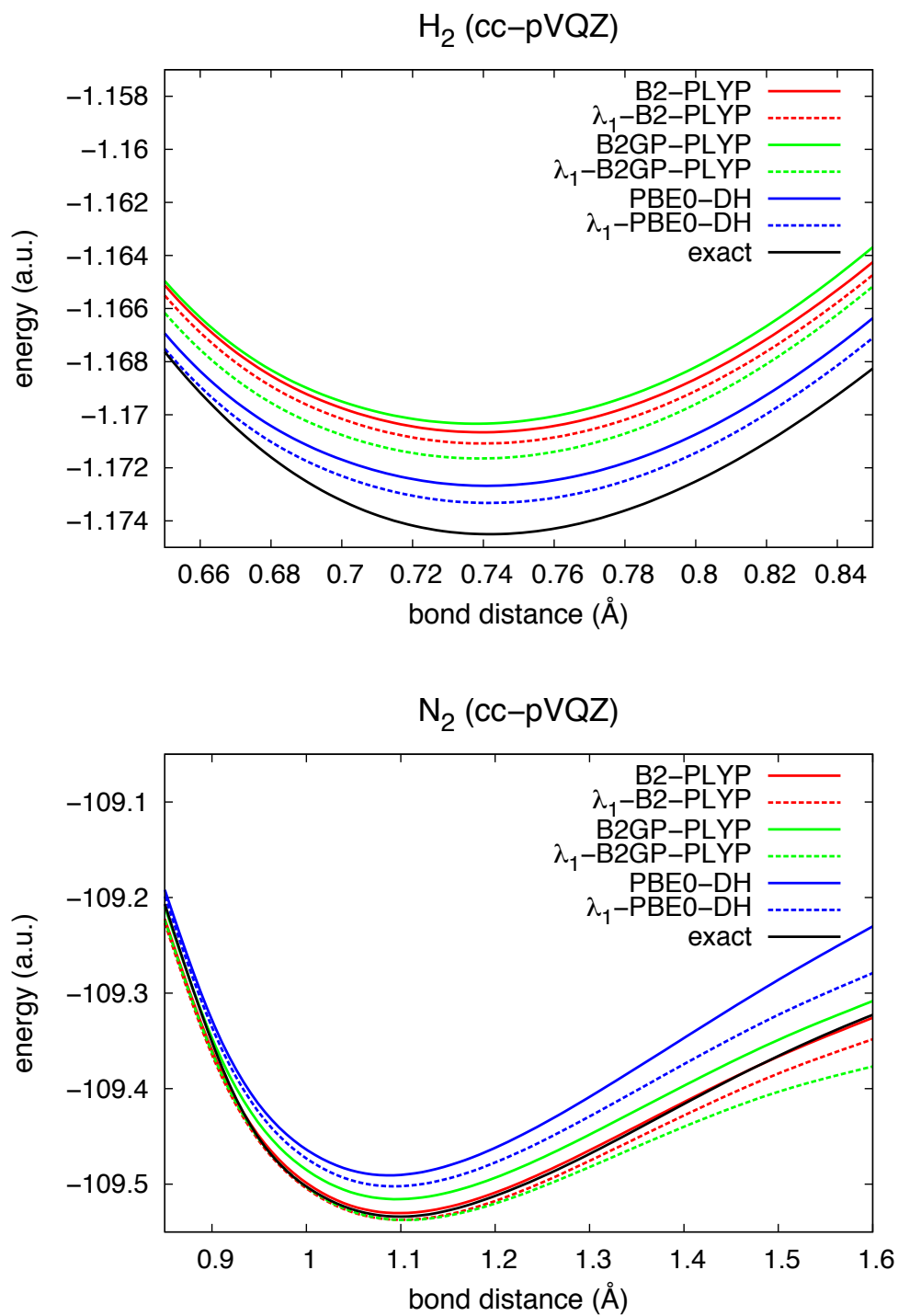


FIG. 2: Fromager, Journal of Chemical Physics

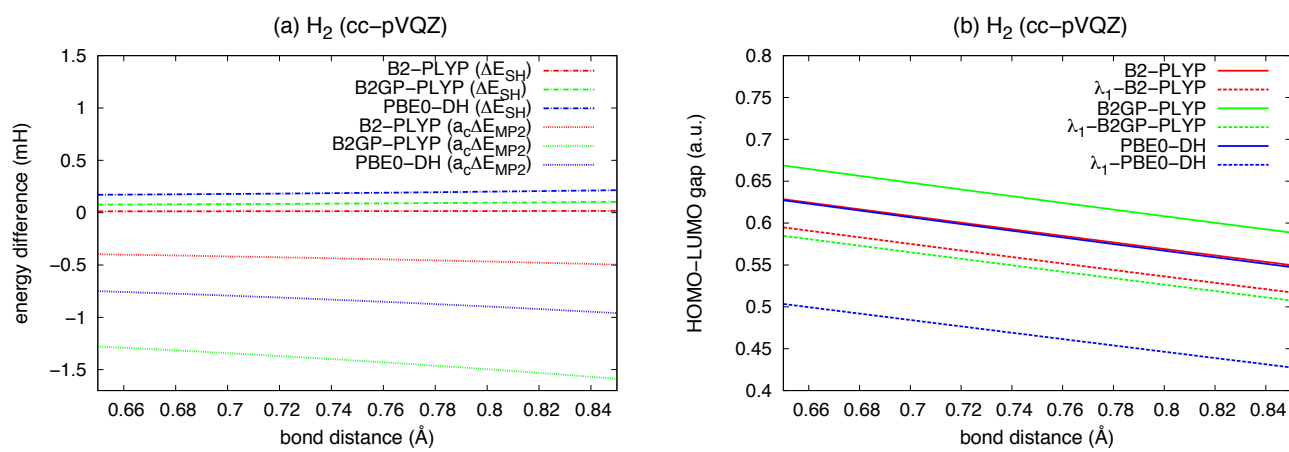
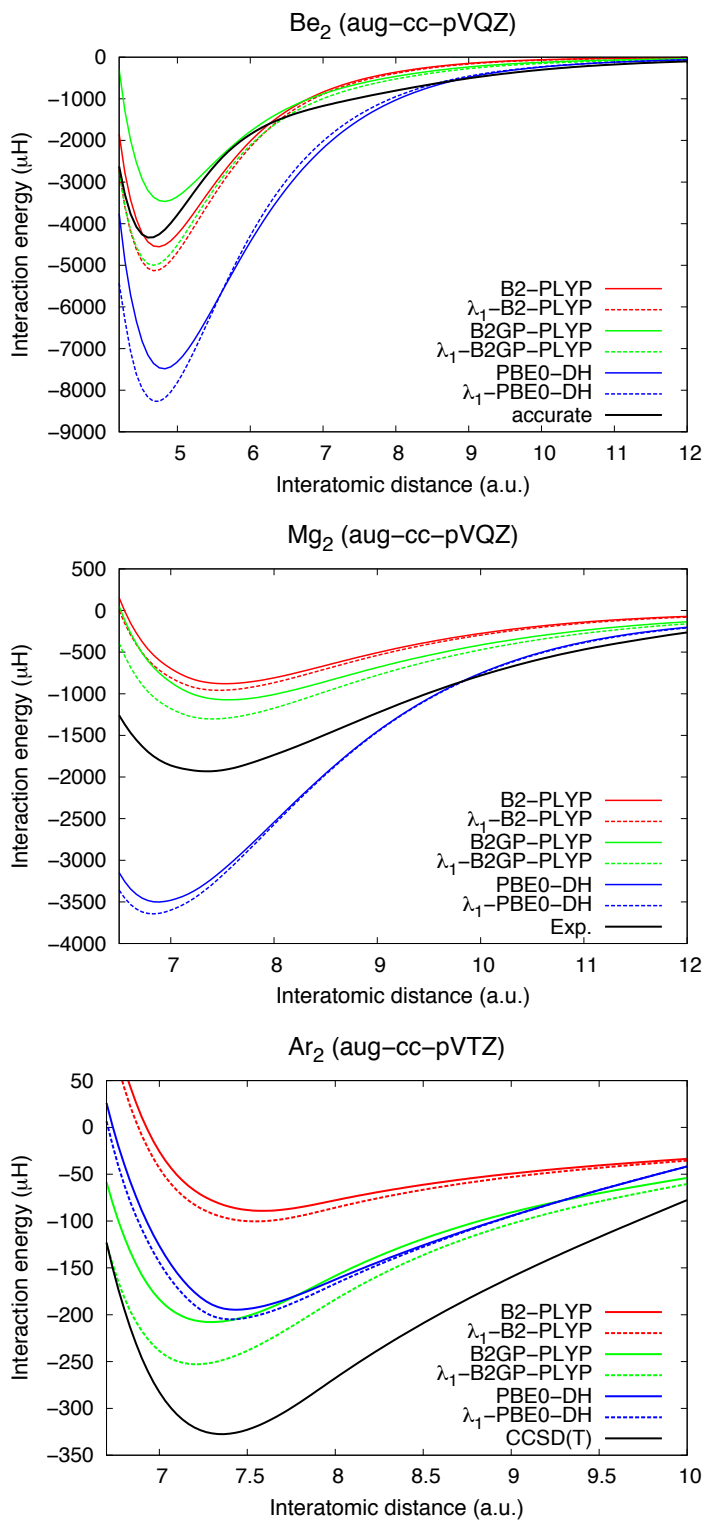


FIG. 3: Fromager, Journal of Chemical Physics



functional	$a_x = \lambda_2$	$a_x^2$	$a_c$	$\lambda_1 = a'_x$	$a'_c$
B2-PLYP <sup>?</sup>	0.53	0.28	0.27	0.43	0.19
B2T-PLYP <sup>?</sup>	0.60	0.36	0.31	0.38	0.14
mPW2-PLYP <sup>?</sup>	0.55	0.30	0.25	0.32	0.10
mPW2K-PLYP <sup>?</sup>	0.72	0.52	0.42	0.41	0.17
B2GP-PLYP <sup>?</sup>	0.65	0.42	0.36	0.40	0.16
B2 $\pi$ -PLYP <sup>?</sup>	0.602	0.362	0.273	0.303	0.092
PBE0-DH <sup>?</sup> ( $a_c = a_x^3$ )	0.50	0.25	0.125	0.146	0.021

TABLE I: Regular ( $a_x$ ,  $a_c$ ) and modified ( $a'_x$ ,  $a'_c$ ) exchange-correlation coefficients corresponding to conventional double hybrids.